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FINAL SUMMARY REPORT

POROUS ELECTRODE STUDIES

by

T. KATAN

Chemistry Department
Lockheed Palo Alto Research Laboratory
Palo Alto, California 94304

July 1980

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FOREWORD

This report is a final report for the work conducted under the Office of Naval Research Contract N00014-73-C-0397 during the period 1973-1980. The report is a summary of the various efforts during this period and acts more as a guide to the assorted publications rather than as a detailed description of all the work. Brevity is maintained, while the concepts and derivable conclusions are recapitulated and reviewed.

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ABSTRACT

This summary report describes the development of experimental analogs of porous electrodes, giving their value in determining reaction profiles and reaction paths. The sphere-bed electrode and single-pore cell analogs are applied to elucidating the reaction modes of the Ag/AgCl, AgO/Ag₂O/Ag, and Zn/ZnO electrodes and to testing various theories that predict electrode behavior.

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1. INTRODUCTION

The Navy requires portable power sources for many applications including communications and ordnance. Both primary and secondary batteries are used, and it is important to have knowledge of the characteristic modes of failure and the effects of discharge on cell performance.

This summary report describes a series of investigations undertaken to ascertain the electrochemical and transport processes occurring within porous electrodes. The reaction modes of the AgCl/Ag and $\text{AgO/Ag}_2\text{O/Ag}$ porous electrode systems are studied using the sphere-bed electrode and single-pore structure methods. A basis is formed for better understanding of the sequence of steps and structural changes occurring during discharge that affect performance.

These studies were conducted at the Lockheed Palo Alto Research Laboratory during the period 1973-1980 under the auspices of the U.S. Navy, Office of Naval Research. During this period, Dr. Theodore Katan was the principal investigator.

In this report, a recapitulation of past accomplishments is presented together with derivable conclusions. Brevity is maintained by reference to earlier publications and reports.

After a statement of the basic problem and goals (Sections 2 and 3), an historical background is developed (Section 4) and connected to the results of this work (Section 5). Lists of the accomplishments in the form of publications, presented papers, and motivation of related work, and personnel are given in Section 6.

2. PROBLEM STATEMENT

The complexities of battery electrode design are evident from consideration of the multitudinous processes occurring during cathode discharge. Commonly, cathodic reaction involves reduction of a sparingly soluble salt or metallic oxide in an electrode, sometimes called an electrode of the "second kind" (Ref. 1). With few exceptions, the active cathodic material is a poor electrical conductor, and a conductive material is needed to channel electron flow to the sites of electrochemical reaction. The surface of the electrical conductor may also provide sites for reduction of either the dissolved or solid reactive species.

A typical cathode or positive electrode for a practical cell therefore consists of a network of conductive material with active reactant distributed throughout the conductive network. The conductive material maintains electron flow while supplying reaction area. Some degree of porosity is required so that electrolyte may contact the reactant in depth to make available a large reaction zone. Also, anodes or negative electrodes can often develop a second solid phase that complicates electrode operation.

It is apparent that correct design should enable optimal balance of electronic, mass, and ionic fluxes and, consequently, of electrode structure and composition which allow for current distribution and morphological changes within the pores. Such a balance is generally not obtained because it is not accurately known. Further, the corrective action needed to impart and retain an optimal structural balance is not clear. Morphological manifestations during discharge or cycling may form a structure which is entirely different from the original one, and the key is to ascertain this change and to design accordingly.

Phenomenological observations when properly made, even without mathematical modeling, can uncover governing stochastic steps in the overall electrode process. The "real world" of actions within the pores should be determined with suitable

experimental analogs so that improvements in electrode design can be based on experimental principles. The approach used here is to determine a rational design by combining elementary concepts derived from past mathematical treatments and a number of experimental analogs of the "real" electrochemical system. Two experimental analogs developed under ONR support are used - the uniform sphere-bed electrode and the analog single-pore cell.

3. PROJECT GOALS

The specific technological goal of the studies given here is to gain knowledge to enable improvements in cycle life, voltage efficiency, electrode capacity, discharge/charge rate, and current density of consumable reactant in battery electrodes.

The general goal is to develop principles of electrode design just as they are for other chemical engineering systems and to provide a set of guidelines for battery manufacture and application. At first, however, clear understanding is necessary of the types of elementary processes occurring within the pores and of corresponding morphological changes which influence transport. Development of theoretical treatment can then be undertaken based on true representations.

It is our purpose to provide the experimental bases for developing principles of battery electrode design closely corresponding to reality. Methods are used for identification and evaluation of local conditions during charge or discharge and for ascertaining current distributions within porous electrode structures. The work is closely coordinated with and, in part, dictated by requirements of theoretical treatments and principles under development primarily by Professor D. N. Bennion, Brigham Young University. Additionally, work is correlated with and assisted by Professor J. Perkins, U. S. Naval Postgraduate School, Monterey, who is engaged in studies on the zinc electrode, and also, collaborations are made with Dr. S. Szpak, Naval Ocean Systems Center, San Diego, on single-pore electrodes.

4. HISTORICAL BACKGROUND

Experimental determinations of current distribution and morphological changes in porous battery electrodes have been considerably limited in the past. For experimental determinations to be useful, currents must be measured and structural changes must be determined at corresponding locations within a small region in electrodes fabricated in series which change monotonically with respect to some structural parameter. Such information is not easily obtained when pores are small, on the order of 1 to 10 microns in effective diameter, and when the systematic and independent change of a single parameter is needed.

Experiments have progressed with idealized single pores whose multiple aggregates are assumed to constitute practical electrodes. Notably, Brodd (Ref. 2) and Szpak et al. (Ref. 3) attempted to provide an experimental basis for theoretical treatments of current distribution in pores larger than 800 microns in diameter, while Will and Hess (Ref. 4) and Diefendorf and Chua (Ref. 5) were more concerned with morphological changes in one-dimensional pores of cadmium/cadmium-hydroxide electrodes. These experimental studies have not found serious application in practical systems, mainly because practical porous electrodes have smaller pores, about 1 micron, and pores in battery electrodes are interconnected and tortuous; a method for translation of results from model experiments to practical electrodes was not known.

More recently, under ONR sponsorship Szpak and Katan (Ref. 6) were able to reduce pore spacing in a single, segmented pore to 60 μm by microelectronic techniques, and they observed the evolution of reaction profile. Similar, corroborative work and theory were developed by Place and Alkire (Ref. 7) in single pores with 250- μm spacing. These reported single-pore techniques merit serious consideration in studying battery electrodes.

The use of aggregates of pores in a model porous electrode was attempted by Alkire et al. (Refs. 8, 9), Bro and Kang (Ref. 10), Nagy and Brockris (Ref. 11), and

Simonsson (Ref. 12). The well-planned experiments of Alkire et al. with the Cu/CuSO_4 electrode encountered unfortunate technical difficulties, although associated theoretical advances have been important (Ref. 8). Bro and Kang (Ref. 10) worked with porous structures closely resembling practical electrodes. They worked with the $\text{Cd}/\text{Cd}(\text{OH})_2$ system using sintered cadmium electrodes of constant thickness and porosity. The electrodes were cut into sections after charging or discharging, and the current distribution was inferred from the amount of chemical change that occurred in each section. The merit of this approach lies in the more direct applicability of empirical results to actual electrodes. Bro and Kang were able to give preliminary mathematical representation to their distribution curves and demonstrated the phenomenon of choking of the first kind; i.e., the blockage of recesses of a porous electrode from current access by products formed in the electrolyte of the pores at the front sections.

Nagy and Bockris (Ref. 11) studied the $\text{Zn}/\text{Zn}(\text{OH})_2$ system with porous zinc electrodes of constant thickness and porosity by analyzing sliced sections after anodic treatment in KOH solutions. They used a scanning electron microscope (SEM) to examine along the edge of some electrodes, actually a region where current distortion is greatest. The zinc oxide film layer on the zinc could be shown, but wide variations of growth patterns were not distinguished. From the determined gradual decrease in reaction with depth into the electrode, Nagy and Brockris (Ref. 11) were able to give elementary mathematical representation and analysis for their observed current distributions.

Simonsson won the young author's award of the Electrochemical Society for his paper on the porous $\text{PbO}_2/\text{PbSO}_4$ electrode (Ref. 12). This careful work contributed much to understanding of current profile laterally within the conducting grid cup which contains PbO reactant. If this Swedish work is continued, much should be learned of the physical nature of PbO_2 in the grid at various stages of discharge and as a function of depth.

The work of Bro and Kang (Ref. 10), Nagy and Brockris (Ref. 11), and Simonsson (Ref. 12) are limited in amount of accumulated data and extent of morphological examination. A wide range of particle sizes was used in the preparation of the utilized porous electrodes so that electrode structures could not be well defined.

In studies of current distribution in porous electrodes, the duration of charge or discharge must remain small compared with the time required for morphological changes which grossly influence distribution; a method for checking the morphological state should be used to assure correct interpretation as well as to determine kinetics of growth and depletion. Additionally, uniformity and simplicity of particle size and shape should be maintained to facilitate analyses. Otherwise, specific surface area will vary considerably within selected small volume elements of the electrode, and, consequently, local current density at a site selected for morphological examination cannot be related to the depth of the site from the front face of the electrode in a regular way. This regular relation is important if morphological development, growth patterns of reaction products and consumed material, is to be followed, understood, and related to dominant transport processes. These conditions have not been followed closely in the past; thus, the usefulness of work has often been restricted.

In the work described here, conducted under the Naval Air Systems Command Contract N00019-71-C-0369 and continued under the Office of Naval Research Contract N00014-73-C-0397, experimental conditions were utilized which met the above criteria and which resulted in some understanding of electrode processes within pores. An experimental electrode was developed (Ref. 13) which could yield data that are both substantial and meaningful, i.e., data from a well-characterized structure consisting of a bed of uniform silver spheres. In addition, a single-pore electrode was developed and used (Ref. 14). A summary of this work on porous electrodes is given in the next section.

5. SUMMARY OF RESULTS

The results are essentially given by the brief descriptions of the publications itemized in Section 6. The publications are also listed as Refs. 6, and 13 to 26 for convenience of presentation. In this section, the accomplishments are organized into various categories rather than chronologically listed as in Section 5, and thus we present the overall development of the work, giving an historical background within the bounds of the ONR-supported work.

5.1 Development of Analog Electrodes

The need for better analog experimental electrodes became apparent as mathematical theories of porous electrodes began to evolve (Refs. 27, 28). The theories had to have a realistic basis, particularly with reference to a recurring mathematical constant, the so-called mass transfer coefficient. Consequently, Dr. H. Rosenwasser, Naval Air Systems Command, supported work at Lockheed on the silver sphere-bed electrode under NAVAIR Contract N00019-71-C-0342 which led to the ONR work reported here.

Silver spheres, obtainable in classified sizes from 10 to 200 μm , were used to construct stationary porous electrode beds. The beds had very low resistivities, ca. $0.02 \Omega \text{ cm}$, as compared to the other metal powder beds. An 1N KCl electrolyte was used with the silver spheres as an anode or cathode because a considerable amount of literature and publications existed for the AgCl/Ag electrode.

The silver sphere-bed proved to be a valuable tool for evaluating reaction paths (Ref. 13) and reaction profiles (Ref. 6). The bed could be easily sectioned after an anodizing step, for example, analyzed and examined with SEM to deduce the evolution of the reaction profile in a porous structure together with accompanying morphological changes.

At the suggestion of Dr. R. Marcus, ONR Office, Pasadena, some work was done with Professor J. Perkins, Naval Postgraduate School, Monterey. Professor Perkins' interest was in the zinc electrode, and a zinc sphere-bed was constructed. The specific resistance was too high, and, instead, the single-pore zinc cell was developed with Lt. J. Savory, a student at Monterey (Ref. 14). This cell permitted optical viewing within a simulated pore through a Lucite cover slide placed over a planar electrode.

The single-pore cell has been a valuable tool for developing understanding of both the zinc (Ref. 14) and nickel electrodes and is the basis for work now in progress at Lockheed under a DOE contract.

5.2 Reaction Paths for the AgCl/Ag Electrode

The transport paths and kinetics were established for the Ag/AgCl porous electrode (Refs. 13, 15). A dissolution/diffusion/deposition mode for both charge and discharge was shown to occur, and distances were measured for dissolution/deposition site separation, density, and size within the pores of a porous electrode structure.

Parameters critical to the application of a comprehensive theoretical representation of a porous battery electrode were thus collected and made available; advantageously, parametric data were collected for a well-known, exhaustively studied electrochemical system, that of Ag/AgCl. Theories can thus be applied which are based on actual physicochemical changes within the pores of a practical electrode - i.e., based on a true representation for the case of a dissolution/diffusion/deposition process in porous battery electrodes.

5.3 Tests of Newman-Bennion Theory

Based on these determined mechanistic parameters, the Newman-Bennion theory of electrode behavior was applied to porous Ag/AgCl electrodes. The electrodes were subjected to slightly different conditions and then sliced into sections which were analyzed to obtain current profiles. Good agreement of theory and experiment was obtained and this materially substantiated the value and applicability of the Newman-Bennion theory to practical battery electrodes (Ref. 21). Prediction now appears possible of the charging capacity and performance if the basic mechanisms are known.

The results constitute a contribution in improving our understanding of an important class of secondary battery electrodes - e.g., the $\text{Cd}/\text{Cd}(\text{OH})_2$ and $\text{PbO}_2/\text{PbSO}_4$ electrodes that operate via the dissolution/diffusion/deposition mode. Studies of this kind which accurately identify kinetic-transport parameters and modes, together with the prediction of corresponding current profiles by rational theory, remain as a future course for improving battery performance.

In the application of the Newman-Bennion theory as well as many others, certain geometrical parameters of the porous structure enter into the mathematical expressions. Somehow the performance of the battery must be related to those parameters of use to the battery manufacturer, such as porosity, pore size, electrode thickness, and specific surface area. Previously, the relation of these geometrical parameters to each other was not clear, and under the ONR-supported work a treatment was developed whereby these could be related and measured in the laboratory (Ref. 18). Parts of this treatment have been applied to the Newman-Bennion theory applied to the Ag/AgCl electrode (Ref. 21).

5.4 Test of Other Theories

Since the pioneer work in 1945 of Daniel-Bek (Ref. 29), the depth of reaction penetration into an electrode was recognized as an important parameter that is connected to the physical structure of the electrode. More recently, De Levie (Ref. 30), under ONR sponsorship, outlined mathematical treatments partly based on this original approach of Daniel-Bek. These theories do not account for the stochastic steps occurring within the electrode, but can account, in a qualitative manner at least, for porous electrode behavior. Stochastic steps can be considered, however, in certain expansions of the treatments. The mathematical expressions are simpler than the more detailed treatments such as those of Newman and Bennion (Refs. 27, 28).

A Daniel-Bek-type treatment was developed in this work which accounted for the movement of reaction fronts into the pore with the passage of time (Ref. 16), i.e., with the discontinuance of one mode of reaction and the onset of another. Reasonable accuracy was shown (Ref. 16), and this phenomenon has now been shown to occur in zinc electrodes (Ref. 31).

More elementary treatments in the prediction of penetration depths have proved surprisingly accurate for a number of structures (Refs. 6, 17, 22). Thus, without the use of computers, predictions now appear possible in relating optimal electrode thickness to other geometrical parameters of porous structures (Ref. 18).

5.5 Ohmic Resistance of Electrode Mixtures

The ohmic resistance of mixtures of particulate conductors and nonconductors was measured and a theory developed for its prediction (Ref. 19). This work has caused considerable interest in the context of predicting conductivity of electrode pastes.

5.6 The Zinc Electrode

In collaborations with Professor J. Perkins of the Naval Postgraduate School, Monterey, and his graduate student, Lt. J. R. Savory, contributions were made on the zinc electrode. Mainly, onset of sudden passivation was related to a simultaneous precipitation of flocculent ZnO , and this passivation was removed by addition of fresh electrolyte, showing the importance of convective stirring through the electrode. In-situ morphological examinations revealed that an irreversible passivation occurred more slowly by covering with a thin, adherent film, and that a dissolution, diffusion, deposition mode prevailed in the formation of ZnO .

It was also shown that zinc dendrite growth during charging was associated with hydrogen gas evolution and that the presence of hydrogen apparently interferes with the cathodic deposition. This work formed the basis of subsequent DOE contracts (see Section 6.4).

5.7 Charge/Discharge Curves During Cycling

From the experience gained with the silver oxide electrode (Refs. 20, 24, 25), under this ONR sponsorship, interpretations could be made of the charge/discharge curves of silver/zinc cells cycled to destruction. It was found that the characteristic shapes of the i - E curves, namely, the Shepherd parameters, were relatively insensitive to prediction of a pending failure. Rather, response times on closing or opening the circuit became slower as the cells aged, and these times could be used as a basis for predicting cell life (Ref. 15).

5.8 The $\text{AgO}/\text{Ag}_2\text{O}/\text{Ag}$ Electrode

Work on the $\text{Ag}/\text{Ag}_2\text{O}$ electrode has revealed that the formation of AgO during charging is from Ag rather than Ag_2O and that a metastable, soluble Ag II species is a precursor to solid AgO formation (Ref. 14). There is a good chance with this work, now in progress, that the solubility of AgO will be determined for the first time as well as the equilibrium constant for the disproportionation of Ag_2O into Ag and AgO . These findings directly bear on the reliability and performance of the numerous DoD silver/zinc batteries now in use and have resulted in an additional subcontract with the U.S. Navy (see Section 6.4).

The effect of light was also studied on $\text{AgO}/\text{Ag}_2\text{O}/\text{Ag}$ electrodes, and it was shown that while the potentials of the various reactions are not changed the rates of the $\text{AgO}/\text{Ag}_2\text{O}$ conversion are changed by incident light (Ref. 25).

5.9 Dental Amalgam Corrosion

The single-pore cell replicates the situation existing between tooth and amalgam restoration, i.e., a crevice on the order of a few microns is formed between tooth and a corroding metal. As such, the cell was used to study the corrosion modes of various dental amalgams to show that the tin-mercury phase undergoes dissolution of tin with a deposition of $\text{SnO} \cdot x\text{H}_2\text{O}$ as a thin adherent film (Ref. 23). This work has resulted in an NIH contract for the College of the Pacific, School of Dentistry (see Section 6.4).

6. LISTS OF PUBLICATIONS AND RELATED MATTERS

This section lists publications and presented papers resulting from the U.S. Navy-sponsored work, and the personnel who were engaged in this work. Included is a list of research and development work sponsored by other agencies but known to have resulted from the technology developed here. A synopsis or title is given for each listed item to explain its connection to the overall goals of this program.

6.1 Publications

1. "Silver/Silver Chloride Electrode: Reaction Paths on Discharge," T. Katan, S. Szpak, and D. N. Bennion, J. Electrochem. Soc. 120, 883 (1973)

This article establishes typical reaction modes for a well-known electrode system and furnishes parameters to test theoretical treatments developed to describe porous electrode behavior (work primarily under NAVAIR Contract N00019-71-C-369).

2. "Silver/Silver Chloride Electrodes: Surface Morphology on Charging and Discharging," T. Katan, S. Szpak, and D. N. Bennion, J. Electrochem. Soc. 121, 757 (1974)

Experimental observations are used to show the importance of surface morphological changes in influencing local reaction kinetics and transport inside porous electrodes, i.e., for dissolution/transport/deposition mechanism.

3. "Silver/Silver Chloride Electrode: Charging of a Porous Structure," S. Szpak, A. Nedoluha, and T. Katan, J. Electrochem. Soc. 122, 1054 (1975)

This work indicates how surface coverage by a nonconducting reaction product can shift the current distribution within porous electrodes and cause a reaction front to proceed within the structure.

4. "Practical Aspects of Electrode Modeling," S. Szpak, T. Katan, and D. N. Bennion, Proc. Ann. Power Sources Conf. 26, 93 (1974)

An outline is given of electrochemical tools available to battery designers and fabricators with examples of their application.

5. "Relating Geometrical Variables of Porous Electrodes," T. Katan and H. F. Bauman, J. Electrochem. Soc. 122, 77 (1975)

The essential geometrical parameters of porous structures are identified and related to serve as a guide in the design and fabrication of porous electrodes.

6. "Electrical Conductivity of Particulate Mixtures," T. Katan and S. Szpak, J. Electrochem. Soc. (in preparation)

Electrical conductivity is determined as a function of composition for porous structures consisting of mixtures of conducting and poorly-conducting particles, i.e., both experimentally and theoretically, to indicate occurrence and reasons for apparent anomalous behavior.

7. "An Experimental Study of Reaction Profiles in Porous Electrodes," S. Szpak and T. Katan, J. Electrochem. Soc. **122**, 1063 (1975)

The evolution of reaction profile is experimentally determined, showing the interplay between choking of the first and second kinds in porous structures as concentration and current density are changed, and a new model electrode system is introduced.

8. "Analysis of Porous Electrodes with Sparingly Soluble Reactants, IV. Application to Particulate Bed Electrode: Ag/AgCl System," T. Katan, H. Gu, and D. N. Bennion, J. Electrochem. Soc. **123**, 1370 (1976)

The Dunning-Bennion-Newman theory was tested in a sequence of experiments with bed-electrodes consisting of uniform silver spheres and found to have prognostic value as well as good applicability for a porous electrode with sparingly-soluble product.

9. "Detection of Elementary Processes Within Porous Electrodes," S. Szpak and T. Katan, Proc. Symp. Energy Storage and Conversion, the Electrochemical Society **77-6**, 770 (1977)

The optimum thickness of porous electrodes is theoretically related to the electrodes' structural variables such as specific surface area and porosity, and the effects on optimum thickness of an onset of competing consecutive reactions is found. The optimum thicknesses of three experimental electrodes are determined and found to agree with theory to within ± 30 percent.

10. "Observations of an Operating Zinc-Pore Electrode," T. Katan, J. R. Savory, and J. Perkins, J. Electrochem Soc. **126**, 1835 (1979)

Morphological changes occurring within a zinc pore during charge and discharge are described. Evidence is presented that harmful zinc dendrite growth is caused by the presence of hydrogen, and the exchange current density for zinc in 10 N KOH is measured as $6.4 \times 10^{-2} \text{ A cm}^{-2}$.

11. "Corrosion Penetration in Crevices of Dental Amalgam," T. Katan and G. Ryge, J. Electrochem Soc. **126**, 903 (1979)

The single-pore cell developed under this contract was applied to the study of crevice corrosion in dental amalgams. Evidence is presented that the corrosion product is $\text{SnO} \cdot x\text{H}_2\text{O}$ with $1 < x < 1.5$. The metallic phases present are identified with respect to their role in the corrosion process.

12. "Modes of Charge/Discharge in Porous Ag/Ag₂O Electrodes," T. Katan and K. C. Tsai, J. Electrochem. Soc. (in preparation)

Evidence is found that the first formation of AgO during galvanostatic charge involves a metastable, soluble Ag II species before solid AgO is formed. During charge, formation of this Ag II species and, later, the solid AgO appears to be from Ag rather than from Ag₂O.

13. "Influence of Light on Mode of AgO Discharge," T. Katan and K. C. Tsai, J. Electrochem. Soc. (in preparation)

Light is found to accelerate the decay in open-circuit potential of AgO towards that of Ag₂O. The reverse disproportionation hypothesis is used to explain this phenomenon.

6.2 Presented Papers and Published Extended Abstracts*

1. "Silver/Silver Chloride Electrodes; Surface Morphology on Charging and Discharging," T. Katan, S. Szpak, and D. N. Bennion, The Electrochemical Society, 143rd National Meeting, Chicago, Illinois, 15 May 1973; EAES 73-1, 593 (1973)
2. "Relating Structural Variables of Porous Electrodes," T. Katan and H. F. Bauman, The Electrochemical Society, 145th National Meeting, San Francisco, California, 17 May 1974; EAES 74-1, 842 (1974)
3. "Practical Aspects of Electrode Modeling," S. Szpak, T. Katan, and D. N. Bennion, 26th Power Sources Symposium, Atlantic City, 1 May 1974
4. "Electrical Conductivity of Particulate Mixtures," T. Katan and S. Szpak, The Electrochemical Society, 146th National Meeting, New York, New York, 16 Oct 1974; EAES 74-2, 83 (1974)
5. "Electrolyte Retention at Gas Electrodes," T. Katan and F. M. Gonzalez, A.I.Ch. E., 6th Annual Meeting, Washington, D.C., 2 Dec 1974
6. "Structural Aspects of Porous Electrodes," T. Katan, Electric Power Research Institute (EPRI) Workshop on Methods for Prediction of Optimum Battery Performance, Palo Alto, California, 24 Oct 1974
7. "Experimental Approach to Electrode Modeling," T. Katan and S. Szpak, The Electrochemical Society, 148th National Meeting, Dallas, Texas, 9 Oct 1975, EAES 75-2, 137 (1975)
8. "Analysis of Porous Electrodes with Sparingly Soluble Reactant, IV Application to Particulate Bed Electrode: Ag/AgCl System," T. Katan, H. Gu, and D. N. Bennion, The Electrochemical Society, 148th National Meeting, Dallas, Texas, 9 Oct 1975; EAES 75-2, 135 (1975)

*The letters "EAES" in this list designate "Extended Abstracts of The Electrochemical Society."

9. "Effects of Structure on Porous Electrode Behavior," T. Katan and S. Szpak, The Electrochemical Society, 150th National Meeting, Las Vegas, Nevada, 17 Oct 1976; EAES 76-2, 59 (1976)
10. "Detection of Elementary Processes Within Porous Electrodes," S. Szpak and T. Katan, The Electrochemical Society, 151st National Meeting, Philadelphia, Pennsylvania, 8 May 1977; EAES 77-1, 918 (1977)
11. "Corrosion Penetration in Crevices of Dental Amalgam," T. Katan and G. Ryge, The Electrochemical Society, 152nd National Meeting, Atlanta, Georgia, 10 Oct 1977; EAES 77-2, 291 (1977)
12. "Observations in an Operating Zinc-Pore Electrode," T. Katan, J. R. Savory, and J. Perkins, The Electrochemical Society, 152nd National Meeting, Atlanta, Georgia, 14 Oct 1977; EAES 77-2, 120 (1977)
13. "Morphology of Reduced $\text{Ag}_2\text{O}/\text{Ag}$ and AgO/Ag Surfaces," T. Katan, The Electrochemical Society, 152nd National Meeting, Atlanta, Georgia, 14 Oct 1977; EAES 77-2, 125 (1977)
14. "Crevice Corrosion of Dental Amalgam," T. Katan and G. Ryge, International Association for Dental Research, Copenhagen, Denmark, 14 Mar 1977 (trip paid by University of Pacific)
15. "Nondestructive Testing of Electrochemical Cells," W. C. Spinkler, T. Katan, and H. F. Bauman, The Electrochemical Society, 156th National Meeting, Boston, Massachusetts, 6 May 1979 (partially funded by EPRI); EAES 79-1, 948 (1979)
16. "Characteristic Changes in Charge/Discharge Curves During Cycling," T. Katan, H. F. Bauman, and W. C. Spindler, The Electrochemical Society, 157th National Meeting, Los Angeles, California, 14 Oct 1979 (partially funded by EPRI); EAES 79-2, 449 (1979)
17. "Modes of Charge /Discharge in Porous $\text{Ag}/\text{Ag}_2\text{O}/\text{AgO}$ Electrodes," T. Katan and K. C. Tsai, The Electrochemical Society, 156th National Meeting, Boston, Massachusetts, 6 May 1979; EAES 79-1, 171 (1979)

18. "Influence of Light on Mode of AgO Discharge," T. Katan and K. C. Tsai, The Electrochemical Society, 157th National Meeting, Los Angeles, California, 14 Oct 1979; EAES 79-2, 241 (1979)
19. "Modes of Charge Acquisition and Utilization of Silver Oxide Electrodes," T. Katan and P. J. Bergeron, The Electrochemical Society, 159th National Meeting, Hollywood, Florida, 5 Oct 1980
20. "A Gasometric Method for Analyses of Silver Oxide Electrodes," T. Katan and R. R. Carlen, The Electrochemical Society, 159th National Meeting, Hollywood, Florida, 5 Oct 1980

6.3 Participating Personnel

Personnel who have participated in the conduct of this program are listed below. Those now at the Lockheed Palo Alto Research Laboratory are given first, and the others are given alphabetically.

Dr. Tsai and Mr. Gonzalez were at Lockheed, Dr. Gu was at UCLA, and Lt. Savory was at the Monterey Naval Postgraduate School at the time of their participation.

H. F. Bauman, Staff Scientist
 P. J. Bergeron, Associate Engineer
 R. R. Carlen, Engineer
 A. S. Gleason, Research Engineer
 A. R. Hansen, Senior Research Engineer
 A. H. Heynen, Research Engineer
 T. Katan, Staff Scientist

} Lockheed Palo Alto Research
 Laboratory
 Palo Alto, California

Douglas N. Bennon, Professor
 Brigham Young University
 Salt Lake City, Utah
 F. M. Gonzalez, Legal Consultant
 Amdahl Corporation,
 Sunnyvale, California

Hiram Gu, Scientist
General Motors Corporation
Warren, Michigan

A. Nedoluha, Mathematician
Naval Ocean Systems Center
San Diego, California

J. Perkins, Professor
Naval Postgraduate School
Monterey, California

G. Ryge, Assistant Dean of Research
University of the Pacific
San Francisco, California

J. R. Savory, Lieutenant
U.S. Navy
Stratham, New Hampshire

W. C. Spindler, Contracts Scientist
Electric Power Research Institute
Palo Alto, California

S. Szpak, Staff Scientist
Naval Ocean Systems Center
San Diego, California

K. C. Tsai, Staff Scientist
The Continental Group, Inc.
Cupertino, California

6.4 Initiated Programs

The experimental techniques and approach used under this Navy-sponsored work has resulted in at least four other research and development programs which are listed below. Hopefully, other work not listed here has been stimulated and advanced by the publications and presentations given in the past.

1. DOE Contract EM-78-C-01-5165, "Basic Studies on Nickel-Zinc Batteries," \$73 K, 1979-1980

This program was started because of a unique property of the single-pore cell developed by ONR: in-situ viewing within pores is possible of growing zinc dendrites and hydrogen gas formation at zinc electrodes. Feasibility was proven in the work with Professor Perkins and his student Lt. Savory; see item 10 in the publications list, Section 6.1.

2. DOE Contract LBL 4503610, "Basic Development of Nickel /Zinc Batteries," \$93 K, 1980-1981

This work is a continuation of the program started in item 1 above, still using the same experimental methods.

3. U.S. Navy Contract NOOO3079-C-0068, "Silver/Zinc Cell Phenomenology," ca. \$100 K, 1979-1980

The ONR-supported work on the $\text{AgO}/\text{Ag}_2\text{O}/\text{Ag}$ electrode proved to be very timely in understanding anomalies recently observed in this electrode's performance. In an engineering developmental-oriented program, the ONR studies were continued under the support of the U.S. Navy.

4. NIH Contract, "Corrosion of Dental Amalgam," \$60 K/yr, 1978 - continuous

In collaboration with Professor Gunnar Ryge of the University of the Pacific, School of Dentistry, San Francisco (see item 11 in Section 6.1), advances were made under ONR support in understanding the nature of dental amalgam corrosion. As a result of this effort, support was obtained from NIH for UOP to continue researches on dental amalgam corrosion.

6.5 Award

The work sponsored by the Office of Naval Research under items 2, 3, and 7 in the Publications section, Section 6.1, above was honored with The Electrochemical Society's Battery Division "Research Award." This award was presented to Dr. T. Katan and S. Szpak at the 150th National Meeting in Las Vegas, Nevada, 17 October 1976.

To quote J. Electrochem. Soc. 105, 189C (1958):

"The Research Award of the Battery Division of The Electrochemical Society was established for the purpose of stimulating battery research and encouraging the preparation of high-quality papers for the Journal. It is presented every two years for paper(s) relating to electrochemical cells or batteries. The paper is selected primarily on the basis of scientific merit and importance. This includes originality of concept and experimental approach, thoroughness of experiments, and logic of conclusions. Clarity of presentation also is considered. The Research Award winner is chosen by a committee of five appointed by the Battery Division Chairman, consisting of the Chairman, the Divisional Editor, and three other members of the division. The selection is approved by the Battery Division Executive Committee and the recommendations submitted to the Society Board of Directors for final approval."

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